

REMARKS

Applicants hereby confirm the election of Group I, Claims 1 - 5, which was made by Loretta A. Peters in a telephone conversation with Examiner Moore on April 29, 2003.

Amendments to the Specification

The application Specification has been amended to include subject matter from the commonly-assigned and co-pending U.S. Patent Application Serial No. 10/071,869 , filed February 8, 2002, titled "Halogen-Resistant Anodized Aluminum for Use in Semiconductor Processing Apparatus", which commonly-assigned application was incorporated by reference in its entirety at the time of filing the present application. The commonly-assigned application has common inventors with the present application, and the subject matter of the commonly-assigned application was obviously known in detail to the present inventors. This subject matter is important because it illustrates a particular substrate over which a yttrium oxide coating may be applied to produce the present invention and because it describes the manner in which an anodized coating is applied to advantage prior to application of the yttrium oxide coating. The subject matter added from co-pending U.S. Patent Application Serial No. 10/071,896 is found in the application Specification as originally filed in the following paragraphs: [0021], [0022], [0026], [0027], [0028], [0029], [0041], and [0062].

The application Specification has also been amended to provide a better lead into the paragraph at Page 4, line 21; and, to correct a typographical error which was present at Page 6, line 36.

No new matter has been introduced by the amendment of the Specification as provided above.

Claim Rejections Under 35 USC § 102

Claim 1 is rejected under 35 USC § 102(b) as being anticipated by Japanese Patent Publication No. 3-287797, to Inazawa et al. Applicants obtained a translation of this Japanese Patent Publication to better understand the content of the disclosed subject matter. Enclosed for the Examiner's reference is a copy of the English translation of JP 3-287797 which was obtained by applicants. This translation was prepared by a professional translation service, Ralph McElroy Translation Company of Austin Texas, and is, to the best of applicants' knowledge correct and accurate.

Inazawa et al. pertains to "a corrosion-resistant component material characterized by the fact that, as a corrosion-resistant material having a corrosion-resistant oxidized film formed by the anodic oxidation of the surface of aluminum or an aluminum alloy, after the impregnation of at least one type of ion selected from the group consisting of chromium ions, yttrium ions, zirconium ions, and magnesium ions into the previously mentioned anodically oxidized film, oxides of the impregnated ions are formed inside the previously mentioned anodically oxidized film by carrying out firing." (Claim 1) This process is described at paragraph 4 of Page 4 of the enclosed translation of JP 3-287797. It is clear that any yttrium oxide produced by this method is embedded within the film of anodically oxidized aluminum or aluminum alloy rather than applied over a surface of the anodically oxidized aluminum film.

Inazawa's corrosion-resistant component material is clearly patentably distinguishable in terms of structural composition from the corrosion-resistant component material claimed in applicants' amended and newly added claims. Applicants' amended Claim 1 recites a yttrium oxide coating over an anodized aluminum surface, where the yttrium oxide coating is a spray-coated coating having a mechanically finished surface essentially free from loose particles. Applicants' new independent Claim 13 is also distinguishable over the Inazawa reference in that it recites a processing chamber component resistant to a plasma including fluorine and oxygen species, where the component comprises a high purity aluminum substrate where

particulates formed from mobile impurities have a particle size distribution such that no more than 0.2 % of the particles are larger than 20  $\mu\text{m}$ , with no particles being larger than 50  $\mu\text{m}$ ; an anodized coating on a surface of the high purity aluminum substrate; and a protective coating comprising yttrium oxide overlying the anodized coating.

In light of the amendment to Claim 1, and the distinctions between amended Claim 1 and the Inazawa et al. disclosure, applicants respectfully request withdrawal of the rejection of Claim 1 under 35 USC § 102(b), over Inazawa et al.

#### Claim Rejections Under 35 USC § 103

Claim 2 is rejected under 35 USC § 103(a) as being unpatentable over Inazawa et al., as applied to Claim 1, and further in view of U.S. Patent No. 5,798,016, to Oehrlein et al.

The deficiencies of the disclosure of Inazawa et al. with respect to the patentability of the presently claimed invention are discussed in detail above with respect to the rejection of Claim 1 under 35 USC § 102(b).

Oehrlein et al. is cited by the Examiner as teaching the use of a liner composed of an aluminum alloy and coated with an yttrium oxide coating for use in a processing chamber for the purpose of protecting the walls from plasma generated during an etching process. The Examiner cites Col. 5, lines 24 - 39, of Oehrlein et al., which states as follows: "The liner and/or the walls of the etching chamber for the first and second exemplary embodiments can be constructed from a wide variety of materials, for example, ceramics, aluminum, steel and/or quartz. Aluminum is the preferred material because it is easy to machine. However, aluminum is reactive to the plasma generated from some of the precursor gases used during the etching process. Thus, aluminum oxide or a coating thereof disposed on the liner or chamber walls is used because aluminum oxide is chemically inert to the plasma. In addition to the materials used to construct the liner and/or chamber walls, a protective coating can be applied to the surface of the liner and/or the chamber walls. For example,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , or  $\text{Y}_2\text{O}_3$  may be used as coating materials

for the exposed surfaces. These materials are selected for their etching resistance to the plasma generated during the etching process.”

If one were to combine the teachings of Inazawa et al. with those of Oehrlein et al., prior to application of a yttrium oxide coating, for example, one might be motivated to provide an oxidized coating by first embedding ions into an oxidized aluminum surface, then firing the surface to oxidize the ions. In addition, a reading of Oehrlein et al. alone does not provide a description of a method of application for the potential oxides which are to be used as coating materials. Further, the Oehrlein et al. reference does not even suggest that a spray-coated protective coating requires a mechanical surface finishing to remove loose particles.

With respect to applicants’ Claim 1 and any claims depending therefrom, the Inazawa et al. reference and the Oehrlein et al. reference, alone or in combination do not disclose or even suggest applicants’ invention as claimed in amended Claim 1. The same is true with respect to applicants’ new independent Claim 13 and claims which depend therefrom.

Whether taken alone or in combination, neither Inazawa et al. nor Oehrlein et al. teaches or even suggests applicants’ claimed invention. In light of the above distinctions, applicants respectfully request withdrawal of the rejection of Claim 2 under 35 USC § 103(a), over Inazawa et al., and further in view of Oehrlein et al.

Claims 2 and 3 are rejected under 35 USC § 103(a) as being unpatentable over Inazawa et al., as applied to Claim 1, and further in view of U.S. Patent Publication No. 2001/0003271, to Otsuki.

The deficiencies of the disclosure of Inazawa et al. with respect to the patentability of the presently claimed invention are discussed in detail above with respect to the rejection of Claim 1 under 35 USC § 102(b).

Otsuki pertains to a processing apparatus having a mounted chamber holding a semiconductor wafer and having members for processing the substrate by heating, plasma, and

process gas, or a combination thereof. A film of  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  is formed on an inner wall surface of the chamber and on exposed surfaces of the members within the chamber. (Abstract)

At paragraphs [0043] to [0044], the Otsuki reference teaches: "In the present invention, the film 14 containing a compound of a III-a element is a sprayed film that substantially comprises  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$ . . . . A weight ratio of  $\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3$  of the sprayed film 14 is preferably 0.5 to 4."

With respect to Claim 1 and claims which depend therefrom, the Otsuki reference discusses the spray deposition of a protective film on an inner surface of a processing apparatus, where the film may be  $\text{Al}_2\text{O}_3$  or a composite film of a combination of  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$ . However, there, there is no mention of the application of a spray-coating of this kind over the surface of an already anodized aluminum chamber surface. Upon reading the disclosure of Otsuki reference, one skilled in the art would not be motivated to apply a coating of  $\text{Y}_2\text{O}_3$  over a previously anodically oxidized aluminum surface, as described and claimed by applicants. Further, there is no mention in the Otsuki reference of the use of a mechanical finishing of the surface of the spray-coated material to remove loose particles.

With respect to applicants' independent Claim 13 and claims which depend therefrom, there is no suggestion of the use of a high purity aluminum substrate having a particular particle size distribution, where there is an anodized coating on the aluminum surface and a protective coating comprising yttrium oxide overlying the anodized coating.

If one skilled in the art were to combine the teachings of the Inazawa et al. and Otsuki references, one might be motivated to provide an oxidized coating by first embedding ions into an oxidized aluminum surface, then firing the surface to oxidize the ions, followed by application of a protective spray coating over the oxidized surface. This combination of process steps would not produce the corrosion-resistant component described and claimed by applicants either in terms of structural or chemical composition.

Whether taken alone or in combination, neither the Inazawa et al. nor Otsuki reference teaches or even suggests applicants' claimed invention. In light of the above distinctions, applicants respectfully request withdrawal of the rejection of Claims 2 and 3 under 35 USC § 103(a), over Inazawa et al., and further in view of Otsuki.

Claim 4 is rejected under 35 USC § 103(a) as being unpatentable over Inazawa et al., as applied to Claim 1, and further in view of Japanese Patent Publication No. 2001023908, to Okada et al.

The deficiencies of the disclosure of Inazawa et al. with respect to the patentability of the presently claimed invention are discussed in detail above with respect to the rejection of Claim 1 under 35 USC § 102(b).

Okada et al. is cited by the Examiner as teaching the use of a gate valve of a vacuum processing chamber, where the gate valve is made of an anodized aluminum alloy. Okada et al. is concerned with maintaining a surface roughness (Ry) of a sealing surface of the gate valve below a certain roughness level.

Okada et al. is not related to providing a yttrium oxide coating on an anodized aluminum surface of a semiconductor processing chamber component. If one were to combine the teachings of Inazawa et al. with those of Okada et al., one would be motivated to provide an oxidized coating by first embedding ions into an oxidized aluminum surface, then firing the surface to oxidize the ions. Neither the Inazawa et al. nor Okada et al. reference is enabling for applicants' coating comprising yttrium oxide over an anodized aluminum surface. Further, with respect to Claim 1, there is no mention of a mechanical surface finishing of a protective coating. With respect to applicants' new independent Claim 13, there is no mention of the high purity aluminum substrate having a particular particle size distribution, with an anodized surface on the aluminum substrate and a protective coating comprising yttrium over the anodized surface.

Whether taken alone or in combination, neither the Inazawa et al. nor Okada et al. reference teaches or even suggests applicants' claimed invention. In light of the above distinctions, applicants respectfully request withdrawal of the rejection of Claim 4 under 35 USC § 103(a), over Inasawa et al., and further in view of Okada et al.

Claim 5 is rejected under 35 USC § 103(a) as being unpatentable over Inazawa et al., as applied to Claim 1, and further in view of U.S. Patent No. 6,521,046, to Tanaka et al.

The deficiencies of the disclosure of Inazawa et al. with respect to the patentability of the presently claimed invention are discussed in detail above with respect to the rejection of Claim 1 under 35 USC § 102(b).

Tanaka et al. is cited by the Examiner as teaching a high purity anodized aluminum alloy. However, the teachings of a combination of the Inazawa et al. and Tanaka et al. references teaches away from the value of the use of a high purity aluminum alloy as taught by applicants, teaching the embedding of impurity ions within the surface of the aluminum substrate, followed by oxidation of these ions to produce compounds. With respect to applicants' Claim 1 and claims which depend therefrom, a combination of the Inazawa et al. reference with the Tanaka et al. reference does not even suggest an aluminum substrate having an anodized surface with a yttrium-comprising coating overlying the anodized surface, where the surface of the yttrium-comprising coating has been mechanically finished to remove loose particles. With respect to applicants' independent Claim 13 and claims which depend therefrom, a combination of these references does not even suggest a high purity aluminum substrate having a controlled particle size distribution, an anodized coating on a surface of the high purity aluminum substrate, and a protective coating comprising yttrium oxide overlying the anodized coating.

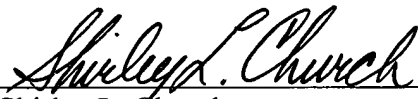
Whether taken alone or in combination, neither the Inazawa et al. nor Tanaka et al. reference teaches or even suggests applicants' claimed invention. In light of the above

distinctions, applicants respectfully request withdrawal of the rejection of Claim 5 under 35 USC § 103(a), over Inasawa et al., and further in view of Tanaka et al.

Applicants believe that the presently pending claims as amended are in condition for allowance, and the Examiner is respectfully requested to enter the present amendments and to pass the application to allowance.

The Examiner is invited to contact applicants' attorney with any questions or suggestions, at the telephone number provided below.

Respectfully submitted,

  
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Japanese Kokai Patent Application No. Hei 3[1991]-287797

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## JAPANESE PATENT OFFICE

## PATENT JOURNAL (A)

KOKAI PATENT APPLICATION NO. HEI 3[1991]-287797

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## CORROSION-RESISTANT COMPONENT MATERIAL

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Agents:	Kuro Fukami, patent attorney, and two others

### Claims

1. A corrosion-resistant component material characterized by the fact that, as a corrosion-resistant component material having a corrosion-resistant oxidized film formed by the anodic oxidation of the surface of aluminum or an aluminum alloy, after the impregnation of at least one type of ion selected from the group consisting of chromium ions, yttrium ions, zirconium ions and magnesium ions into the previously mentioned anodically oxidized film, oxides of the impregnated ions are formed inside the previously mentioned anodically oxidized film by carrying out firing.

2. A corrosion-resistant component material characterized by the fact that, after submersion in or coating of a solution a ceramic precursor consisting of a polymerizable organic metal compound on the outer layer of the corrosion-resistant component material of Claim 1, an insulating film of oxide ceramic is formed by a heat treatment.

3. The corrosion-resistant component material described in Claim 2, in which the previously mentioned polymerizable organic metal compound is a metal alkoxide or a carboxylic acid metal salt.

4. The corrosion-resistant component material described in Claim 2, in which the previously mentioned polymerizable organic metal compound contains at least one metal selected from the group consisting of silicon, aluminum, yttrium, zirconium and magnesium.

### Detailed explanation of the invention

#### Industrial application field

The present invention relates to corrosion-resistant component materials, electric wires, and so on for use in a semiconductor manufacturing apparatus, a vacuum device or the like using a corrosive gas.

#### Prior art and problems to be solved by the invention

Aluminum and aluminum alloys possess a relatively good corrosion resistance. However, if they are used as electric wires or various component materials in a semiconductor manufacturing apparatus or a vacuum device, corrosion proceeds quickly and cracks form due to corrosive vapors of low melting point metals, highly corrosive inorganic halides, raw material gases of organic metal compounds and so on used in chemical vapor deposition, etc. Therefore, the anodic oxidation treatment of electric wires and various component materials has been attempted. By carrying out this treatment, anodically oxidized films are formed on the electric wires or various component materials in order to prevent corrosion. In anodic oxidation, these metals are submerged in a dilute sulfuric acid or other electrolyte aqueous solution according to a conventional method. For the electric wires or various component materials on which the

anodically oxidized films have been formed in this manner, some improvement in corrosion resistance is observed. However, they do not have a sufficient corrosion resistance.

Therefore, the objective of the present invention is provide a corrosion-resistant component material having a sufficient corrosion resistance with respect to corrosive vapors of low melting point metals, highly corrosive inorganic halides, organic metal compounds and so on for use as electric wires or various component materials using aluminum or an aluminum alloy.

#### Means to solve the problems

The corrosion-resistant component material according to Claim 1 is characterized by the fact that, as a corrosion-resistant component material having a corrosion-resistant oxidized film formed by the anodic oxidation of the surface of aluminum or an aluminum alloy, after the impregnation of at least one type of ion selected from the group consisting of chromium ions, yttrium ions, zirconium ions and magnesium ions into the previously mentioned anodically oxidized film, oxides of the impregnated ions are formed inside the previously mentioned anodically oxidized film by carrying out firing.

The corrosion-resistant component material according to Claim 2 is characterized by the fact that, after submersion in or coating of a solution of a ceramic precursor consisting of a polymerizable organic metal compound on the outer layer of the corrosion-resistant component material of Claim 1, an insulating film of the oxide ceramic is formed by a heat treatment.

The insulating film of oxide ceramic is formed by virtually any type of metal oxide. If examples of its materials are given,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_4$ ,  $\text{TiO}_2$ ,  $\text{MgO}$  and so on are available.

Furthermore, as the polymerizable organic metal compound, it is preferable to use a metal alkoxide or a carboxylic acid metal salt. In the case of using a metal alkoxide, the solution of the ceramic precursor is a substance obtained by the addition of a metal alkoxide to an alcohol or other organic solution. Furthermore, if necessary, water and a catalyst are added. As the metal alkoxide, for example, metal ethoxides, propoxides, butoxides and so on can be used preferably. On the other hand, in the case of using a carboxylic acid metal salt, the solution of the ceramic precursor is a substance obtained by the dissolution of a carboxylic acid metal salt in an appropriate organic solvent. In the method using the precursor solution of this type, ceramics are formed by pyrolysis after submersion or coating. For this purpose, it is necessary that the decomposition temperature of the polymerizable organic metal compound is lower than its boiling point or sublimation point. As the carboxylic acid metal salts, specifically, for example, metal salts of naphthenic acid, caprylic acid, stearic acid, and octanoic acid are preferred.

Furthermore, it is preferable that the polymerizable organic metal compound contains at least one metal selected from the group consisting of silicon, aluminum, yttrium, zirconium and magnesium.

#### Function

If at least one of the group of ions consisting of chromium ions, yttrium ions, zirconium ions and magnesium ions is impregnated into the anodically oxidized film and subjected to a heat treatment, the ions that have entered the film will bond well with the anodically oxidized film while it is being oxidized. An  $(\text{AlCr})_2\text{O}_3$  solid solution with low structural defects will be formed. This structure with low defects is considered to cause an improvement in corrosion resistance.

Furthermore, if the insulating film of the oxide ceramic is formed by the heat treatment after the submersion in or the coating of the solution of the plastics precursor following the dispersion of the oxide of the impregnated ions into the anodically oxidized film, high insulating characteristics can be rendered to the corrosion-resistant component material. In addition, the anodically oxidized film that is originally porous can be made dense, and the corrosion resistance is further improved.

#### Application example

1 m of pure aluminum wire with a diameter of 2 mm was submerged in 15 wt% dilute sulfuric acid maintained at 10°C. It was subjected to anodic oxidation by the application of a positive voltage to the aluminum base material at a bath current density of 50 A/dm<sup>2</sup> for two min. An anodically oxidized film of about 10 μm was formed on this wire material. Next, after submersion in a 20 wt% chromium trioxide aqueous solution for 10 min or so, it was dried with a hot air flow at 150°C. After carrying out five cycles of submersion and drying at 150°C, the wire material was further dried in an oxygen gas stream at 500°C.

The surface of this wire material was analyzed with an energy dispersion type fluorescence X-ray spectroscopic analyzer. The surface composition was Al = 84 atom% and Cr = 16 atom%. After this wire material had been placed in a container with a gallium partial pressure controlled at 10 mm Torr for 30 h, the depth of the corrosion pits present on the wire material surface was determined from the cross-sectional observations. The average value was 2 μm. For comparison, a pure aluminum base material without carrying out the anodic oxidation and an anodically oxidized aluminum base material without chromic acid impregnation were placed under the same corrosive environment for 30 h. For the pure aluminum base material, the depth of the corrosion pits was 10 μm or so. For the anodically oxidized aluminum, corrosion

pits of 5  $\mu\text{m}$  were observed in the anodically oxidized film. Thus, the corrosion-resistant aluminum wire of the present invention has a good corrosion resistance.

Furthermore, the corrosion-resistant electric wire on which the anodically oxidized film with added chromium oxide was formed was submerged in a solution obtained by the addition of 1.2N concentrated nitric acid at 1/100 mol with respect to tetrabutyl orthosilicate to a solution obtained by mixing 8 mol% tetrabutyl orthosilicate, 32 mol% water, and 60 mol% ethanol, followed by heating and stirring at 70°C for 2 h. Then, the process of heating at 400°C for 10 min was repeated 10 times. Finally, it was heated in an oxygen gas stream at 500°C for 10 min.

In doing this, an insulating film of silicon oxide was formed at about 5  $\mu\text{m}$  or so on the corrosion-resistant electric wire. The corrosion-resistant electric wire obtained in the manner described previously had an insulation destruction voltage of 600 V. Furthermore, even when this insulation-coated electric wire was wound on a circular cylinder with a diameter of 5 cm, the coating did not crack at all. This wire material was placed in a container with a gallium partial pressure controlled at 10 mm Torr for 30 h. Virtually no corrosion pits were observed on the wire material surface.

#### Effects of the invention

As explained previously, the present invention is a material that possesses excellent corrosion resistance. Thus, the present invention may be effectively used in a component material that is exposed to corrosive vapors of low melting point metals, highly corrosive inorganic halides, organic metal compounds and so on inside a semiconductor manufacturing apparatus or a vacuum plant.

⑩ 日本国特許庁(JP)

⑪ 特許出願公開

⑫ 公開特許公報(A)

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⑭ 公開 平成3年(1991)12月18日

審査請求 未請求 請求項の数 4 (全3頁)

⑮ 発明の名称 耐食部材

⑯ 特 願 平2-89868

⑰ 出 願 平2(1990)4月3日

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## 明 細 書

## 1. 発明の名称

耐食部材

## 2. 特許請求の範囲

(1) アルミニウムまたはアルミニウム合金の表面を陽極酸化させて形成した耐食性の酸化皮膜を有する耐食部材であって、前記陽極酸化皮膜中に、クロムイオン、イットリウムイオン、ジルコニウムイオンおよびマグネシウムイオンからなる群より選ばれた少なくとも一種のイオンを含浸させた後、焼成を行なうことにより、前記陽極酸化皮膜中に含浸させたイオンの酸化物を形成させたことを特徴とする耐食部材。

(2) 請求項1からなる耐食部材の外層に、重合性有機金属化合物からなるセラミックス前駆体の溶液を浸漬もしくは塗布した後、加熱処理することにより、酸化物セラミックスの絶縁膜を形成させたことを特徴とする耐食部材。

(3) 前記重合性有機金属化合物が、金属アルコキシドまたは金属のカルボン酸塩である請求

項2に記載の耐食部材。

(4) 前記重合性有機金属化合物が、珪素、アルミニウム、イットリウム、ジルコニウムおよびマグネシウムからなる群より選ばれた少なくとも一種の金属を含むことを特徴とする請求項2に記載の耐食部材。

## 3. 発明の詳細な説明

## 〔産業上の利用分野〕

この発明は、腐食性ガスを使用する半導体製造装置や真空プラント等に使用する耐食性の部材および電線などに関するものである。

## 〔従来技術および発明が解決しようとする課題〕

アルミニウムおよびアルミニウム合金は、比較的耐食性に優れている。しかし、これらを半導体製造装置中や真空プラント中で、電線や各種の部材として用いると、化学蒸着法等で使用する低融点金属の腐食性蒸気や腐食性の高い無機ハロゲン化合物ならびに有機金属化合物の原料ガス等によって、腐食が早期に進行し、クラックが成長する。このため、電線や各種の部材に陽極酸化処理を施

## 特開平3-287797(2)

すことが試みられている。これは、処理を施すことによって電線や各種の部材に陽極酸化皮膜を形成させ、この皮膜によって腐食の進行を食い止めようとするものである。陽極酸化では、通常の方法に従い、これらの金属を希硫酸等の電解質水溶液中に浸漬し、アノード分極する。しかしながら、このようにして陽極酸化皮膜を形成させた電線および各種の部材は、耐食性の向上が若干見られるものの十分な耐食性を備えたものではなかった。

それゆえに、この発明の目的は、アルミニウムまたはアルミニウム合金を用いた電線や各種の部材において、低融点金属の腐食性蒸気、腐食性の高い無機ハロゲン化合物および有機金属化合物などに対する十分な耐食性を備えた耐食部材を提供することにある。

## [課題を解決するための手段]

請求項1に従う耐食部材は、アルミニウムまたはアルミニウム合金の表面を陽極酸化させて形成した耐食性の酸化皮膜を有する耐食部材であって、陽極酸化皮膜中に、クロムイオン、イットリウム、

ジルコニウムイオンおよびマグネシウムイオンからなる群より選ばれた少なくとも一種のイオンを含浸させた後、焼成を行なうことにより、陽極酸化皮膜中に含浸させたイオンの酸化物を形成させたことを特徴としている。

請求項2に従う耐食部材は、請求項1からなる耐食部材の外層に、重合性有機金属化合物からなるセラミックス前駆体の溶液を浸漬もしくは塗布した後、加熱処理することにより、酸化物セラミックスの絶縁膜を形成させたことを特徴としている。

酸化物セラミックスの絶縁膜はほとんどすべての金属酸化物系セラミックスによって形成できるが、その材質について例を挙げれば、 $\text{SiO}_2$ 、 $\text{Al}_2\text{O}_3$ 、 $\text{ZrO}_2$ 、 $\text{TiO}_2$  および  $\text{MgO}$  等がある。

また、重合性有機金属化合物として、金属アルコキシドまたは金属のカルボン酸塩を用いることが好ましい。金属アルコキシドを用いる場合、セラミックス前駆体の溶液は、アルコール等の有機

溶液に金属アルコキシドを添加したものである。また、必要に応じてこれに水および触媒を添加する。金属アルコキシドとしては、たとえば、金属のエトキシド、プロポキシドおよびブトキシド等がよく用いられる。一方、金属のカルボン酸塩を用いる場合、セラミックス前駆体の溶液は、金属のカルボン酸塩を適当な有機溶媒に溶解したものである。このタイプの前駆体溶液を用いる方法では、浸漬もしくは塗布後に加熱して熱分解することによりセラミックスを生成させていく。このため、用いる重合性有機金属化合物の分解温度は、その沸点やあるいは昇華点よりも低いことが必要である。金属のカルボン酸塩として具体的には、たとえば、ナフテン酸、カプリル酸、ステアリン酸およびオクチル酸の金属塩が好ましい。

また、重合性有機金属化合物は、珪素、アルミニウム、イットリウム、ジルコニウムおよびマグネシウムからなる群より選ばれた少なくとも一種の金属を含むものが好ましい。

## [作用]

陽極酸化皮膜中にクロムイオン、イットリウムイオン、ジルコニウムイオンおよびマグネシウムイオンのうち少なくとも一種を含浸させ加熱処理すると、被膜中に入り込んだイオンは、酸化されながら陽極酸化皮膜と良好に結合し、構造に欠陥の少ない  $(\text{Al}, \text{Cr})_2\text{O}_3$  の固溶体を形成する。この欠陥の少ない構造が、耐食性を向上させると考えられる。

また、陽極酸化皮膜中に含浸イオンの酸化物を分散させた後、セラミックス前駆体の溶液を浸漬もしくは塗布して加熱処理することにより酸化物セラミックスの絶縁膜を形成すれば、耐食部材に高い絶縁性を付与することができるほか、元来多孔性である陽極酸化皮膜を緻密化し耐食性もさらに向上する。

## [実施例]

線径 2 mm  $\phi$  の純アルミニウム線 1 m を温度を 10℃ に保持した 15 重量% 希硫酸中に浸漬しアルミニウム基材に正の電圧を印加して浴電流密度 50 A/dm<sup>2</sup> で 2 分間陽極酸化した。この線材



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には、陽極酸化皮膜が約 $10\mu\text{m}$ 程度形成した。次に、20重量%の三酸化クロムの水溶液中に10分程度浸漬した後、 $150^\circ\text{C}$ の熱風で乾燥した。浸漬および $150^\circ\text{C}$ の乾燥の工程を5回行った後、その線材をさらに酸素気流中 $500^\circ\text{C}$ で乾燥した。

この線材の表面をエネルギー分散型蛍光X線分光分析装置で分析したところ表面組成は、 $\text{Al} = 84\text{atom}\%$ 、 $\text{Cr} = 16\text{atom}\%$ であった。この線材を、 $10\text{mm Torr}$ のガリウム分圧で制御された容器内に30時間放置した後、線材表面に存在する腐食孔の深さを横断面観察より求めたところ、平均値で $2\mu\text{m}$ であった。また比較のため、陽極酸化を行なう前の純アルミニウム基材と、クロム酸浸漬前の陽極酸化したアルミニウム基材を同様の腐食環境下に30時間放置したところ、純アルミニウム基材に関しては腐食孔の深さは $10\mu\text{m}$ 程度であり、陽極酸化アルミニウムに関しては陽極酸化皮膜中に $5\mu\text{m}$ の腐食孔が観察された。このようにこの発明の耐食アルミニウム線は、良好な耐食性を有していた。

また、陽極酸化皮膜中に酸化クロムを形成させた耐食電線を、テトラブチルオルトシリケート8モル%、水32モル%、エタノール60モル%混合した溶液に、1.2Nの濃硝酸をテトラブチルオルトシリケートに対し100分の1モル添加し $70^\circ\text{C}$ で2時間加熱攪拌することにより得た液に浸漬した後、 $400^\circ\text{C}$ で10分間加熱する工程を10回繰返し、最後に $500^\circ\text{C}$ で酸素気流中で10分間加熱を行なった。

このようにして耐食電線上に酸化珪素の絶縁膜が $5\mu\text{m}$ 程度形成された。以上のようにして得られた耐食電線は絶縁破壊電圧が $600\text{V}$ であり、さらに直径 $5\text{cm}$ の円筒にこの絶縁被覆電線を巻きつけても被覆に何ら亀裂が発生しないものであった。この線材を、 $10\text{mm Torr}$ のガリウム分圧で制御された容器内に30時間放置したが、線材表面に存在する腐食孔はほとんど観察されなかった。

## 【発明の効果】

以上説明したように、この発明は耐食性に非常

に優れたものである。したがって、この発明を、半導体製造装置中や真空プラント中で低融点金属の腐食性蒸気や腐食性の高い無機ハロゲン化物ならびに有機金属化合物等にさらされる部材に使用すれば有効である。

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